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INTERMOLECULAR POTENTIAL OF KRYPTON AND XENON ON THE CORE MODEL

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ABSTRACT The potential parameters for the core model have been obtained for krypton and xenon by using simultaneously the viscosity and the second virial coefficient data. The potential energy curves thus obtained are quite close to the elaborate six-parameter of Guggenheim and McGlashan. The satisfactory agreement between the experimental data and the calculated values and the comparatively simple form of the core potential raise the possibility of using it in the place of more commonly used Lennard-Jones (12 6) and exp-6 potentials.

The limitations of the comparatively simple intermolecular potentials like Lennard-Jones (12 6) and the exp-6 models are now well recognised (Kihara 1953, 1955; Guggenheim and McGlashan 1960). However, more elaborate and complicated potentials (e g. six-parameter potential of Guggenheim and McGlashan) are not convenient particularly for the calculation of collision integrals for representing transport properties of gases. Consequently it is necessary to obtain an intermolecular potential model which is comparatively simple in form and at the same time represent the potential adequately. Recent calculation by Barker (1964) for argon on the core model of Kihara is fairly successful in these regards. The core potential with a spherical core of diameter $2a$ may be represented as,

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma-2a}{r-2a}\right)^{12} - \left(\frac{\sigma-2a}{r-2a}\right)^{6}\right] \qquad r > 2a \qquad \ldots \quad (1a)$$

$$\phi(r) = \infty \qquad r \leqslant 2a \qquad \ldots \quad (1b)$$

where σ is the value of r for which $\phi(r) = 0$ and ϵ is the depth of the potential well. The addition of the term a makes the core potential more flexible than the Lennard-Jones (12 6) potential and at the same time the mathematical simplicity is retained. Kihara (1953) obtained the second virial coefficient $B(T)$ on the core model and very recently Barker (1964) has obtained the collision integrals on this model. By combining $B(T)$ and the viscosity data Barker (1961) has obtained the force constants for argon on the core model and the potential energy curve thus obtained is quite close to the elaborate six-parameter potential of Guggenheim and McGlashan (1960). The constants thus obtained can explain all the gaseous properties of argon satisfactorily. The success achieved for argon with the core model raises the possibility of replacing the Lennard-Jones (12 : 6) potential by

the core potential Consequently, we have thought it worthwhile to obtain the intermolecular potentials of Kr and Xe on the core model and test its suitability Recently, Sherwood and Prausnitz (1964) have obtained the force constants for the inert gases on the core model. However as shown by Keller and Zumino (1959) $B(T)$ data alone cannot determine the force parameters uniquely In this paper we have calculated the force parameters for krypton and xenon by utilising both second virial coefficient and viscosity data The constants thus obtained have been checked by calculating various other properties

CALCULATION AND RESULTS

For the determination of the force parameters we shall use simultaneously the second virial coefficient and the viscosity data The viscosity η may be represented as (Hirschfelder Curtiss and Bird)

$$\eta \times 10^7 = 226.93 \frac{\sqrt{MT}}{\sigma^2 \Omega^{(2,2)*}(T^*)} \quad \ldots (2)$$

where M is the molecular weight and $\Omega^{(2,2)}(T^*)$ is a collision integral as calculated by Barker (1964) The second virial coefficient $B(T)$ may be written as,

$$B(T) = b_0 B^*(a^*, T^*) \quad (3)$$

where
$$b_0 = \frac{2\pi N\sigma^3}{3}, \quad a^* = \frac{2a}{\sigma}, \quad T^* = \frac{KT}{\epsilon} \quad (4)$$

and
$$B^*(a^*, T^*) = [2^{\frac{1}{2}} F_3(T^*) + 3.2^{1/3} \cdot a^* F_2(T^*) + 3\, 2^{1/6} \cdot a^{*2} \cdot F_1(T^*) + a^{*3}](1 + a^*)^{-3} \quad (5)$$

$$F_s(T^*) = -\frac{s}{12} \sum_{j=0}^{\infty} \frac{2^j}{j!} \Gamma\left(\frac{6j-s}{12}\right) T^{*-\frac{6j+s}{12}} \quad (6)$$

From Eqs (2) and (3)

$$\log_{10}\left(\frac{\eta\beta}{T^{\frac{1}{2}}}\right) = \log_{10} \frac{B^*(a^*, T^*)}{\Omega^*(a^*, T^*)} + \log \sigma + \log c \quad (7)$$

where
$$c = 266.93 \times \frac{\epsilon}{3} \pi N \sqrt{M} \times 10^{-7}$$

and
$$\log T = \log T^* + \log \frac{\epsilon}{K} \quad \ldots (8)$$

For a chosen value of a^* it is possible to determine σ and ϵ/K from Eqs (7) and (8) by the graphical method (Mason and Rice 1954) The set of values of a^* ϵ/K σ which represented the experimental data best were taken as the correct force parameters The results thus obtained are shown in Table 1 The potential energy curves for krypton and xenon as obtained on the core model are shown together with those for the Lennard-Jones (12 6) and the six-parameter potentials are shown in Figs 1 and 2

COMPARISON WITH EXPERIMENT

(a) *Krypton*

The average deviation between the experimental and the calculated values of the thermal conductivity (Kannuluik and Carman, 1952 temperature range 195° to 579°K) and viscosity (Clifton 1963 temperature range 300° to 690°K) is 0 8% and 2% respectively. Upto 473°K the agreement with the experimental second virial coefficient data is within 2% The agreement becomes worse at higher temperatures This probably means that the effective core diameter is changed at higher temperatures. For all these properties the agreement with the experimental values is better than that obtained by using the constants obtained by Sherwood and Prausnitz (1964) from the second virial coefficient data only.

(b) *Xenon*

For xenon the average deviation between the experimental and the calculated values of thermal conductivity (Kannuluik and Carman, 1952) and viscosity (Trautz Max and Roberg Heberling, 1934) is within 4% and 2% respectively In both the cases the calculated values are lower than the experimental values which may be partly due to the fact that xenon always contains a certain percentage of krypton as impurity. For second virial coefficient the agreement between experimental and the calculated values is excellent (average deviation 2%) over the temperature range 290°-573°K It is interesting to note that the agreement with the experimental $B(T)$ data is better than those obtained by using Sherwood and Prausnitz (1964) who used $B(T)$ data for calculating the force parameters.

(c) *Third Virial Coefficient*

It has been pointed out by Graben and Present (1962) that three-body interactions cannot be neglected in the calculation of the third virial coefficient The three body interaction effect has been calculated approximately by Sherwood and Prausnitz (1964) for the core potential The third virial coefficient C may be expressed as the sum of the contributions of pair-wise interactions and the non-additive interactions i.e.

$$C = C^a + \Delta C \qquad \ldots (9)$$

where $$C^a = -\frac{8\pi^2 N^2}{3} \int\int\int f_{12} f_{13} f_{23} r_{12} r_{13} r_{23} dr_{12} dr_{13} dr_{23}. \qquad \ldots (10)$$

$$\Delta C' = \frac{8\pi^2 N^2}{3} \int\int\int \exp\left(-\frac{\Sigma\phi_{ij}}{kT}\right)\left[\exp\left(-\frac{\Delta\phi}{kT}\right) - 1\right] r_{12}^2 r_{13}^2 r_{23}^2 dr_{12} dr_{13} dr_{23} \quad (11)$$

$$f_{ij} = \exp\left(-\frac{\phi_{ij}}{kT}\right) - 1$$

$$\Sigma\phi_{ij} = \phi_{12} + \phi_{13} + \phi_{23} \quad (12)$$

r_{ij} being the distance between molecules i and j. $\Delta\phi$ represent the difference between the three-body interaction energy and the sum of pair energies.

For obtaining $\Delta C'$ Kihara (1958) has expended $\Delta C'$ in terms of the polarizability α which may be written as

$$\Delta C' = \alpha \cdot \left(\frac{\partial \Delta C'}{\partial \alpha}\right)_{\alpha=0} + \ldots \quad (13)$$

neglecting higher terms.

Consequently C' in the reduced form is given by

$$C^* = \frac{C'}{b_0^2} = C^{*\sigma} + \alpha^* \left(\frac{\partial \Delta C^*}{\partial \alpha^*}\right) \quad (14)$$

The quantities $C^{*\sigma}$ and $\alpha^* \cdot \left(\frac{\partial \Delta C^*}{\partial \alpha^*}\right)$ have been tabulated by Sherwood and Prausnitz (1964) for the core potential. The results obtained by us for the third virial coefficient by using the calculated constants are shown in Table II

TABLE I

Force constants for krypton and xenon

Potential form	krypton			xenon		
	σ in Å	$\frac{\epsilon}{k}$ in °K	α^*	σ in Å	$\frac{\epsilon}{k}$ in °K	α^*
Core potential	3·570	204·0	0·125	3·922	300·6	0·2
Lennard-Jones (12–6)	3·61	190	0	4·055	229	0

TABLE II

Third virial coefficient

$T°k$	Krypton		Xenon	
	Calculated (cc/mole)^2	Experimental (cc/mole)^2 (a)	Calculated (cc/mole)^2	Experimental (cc/mole)^2 (b)
298	2626	2614	7941	6077
323	2383	2262	7109	5314
348	2186	2079	6309	4641
373	2033	1915	5721	4120
398	1908	1845	5233	3744
423	1811	1759	4777	3474
448	1721	1671	4444	3244
473	1659	1584	4170	3035
498	1604	1642	3907	2873
523	1553	1579	3710	2688
548	1513	1563	3540	2528
573	1476	1612	3378	2426

(*a*) Beattie, J. A., Brierley, J. S. and Barriault, R. J., 1952.
(*b*) Beattie, J. A., Barriault, R. J., Brierley, J. S., 1951.

DISCUSSION OF RESULTS

From Figs. 1 and 2 it may be seen that the core potential as derived from the gaseous properties is close to the elaborate six-parameter potential of Guggenheim and McGlashan (1960). As also observed by Barker (1964) for argon the potential energy curve as obtained on the core potential is quite different from that on the Lennard-Jones (12–6) potential. The concept of introducing a hard core most probably makes the potential function more flexible and realistic than the more commonly used Lennard-Jones (12–6) and exp-6 potentials. However, since the effective diameter of the hard core should depend on the energy of the colliding molecules i.e. on temperature, the same set of parameters cannot probably represent potential energy curve over a wide range of temperatures.

The calculations performed for krypton and xenon together with results obtained by Barker (1964) for argon show that the core potential can represent the various macroscopic properties satisfactorily. In view of the comparatively simple form of the core potential, it may be possible to use it in place of usual Lennard-Jones (12–6) potential which is too much restricted as pointed out by Guggenheim and McGlashan (1960).

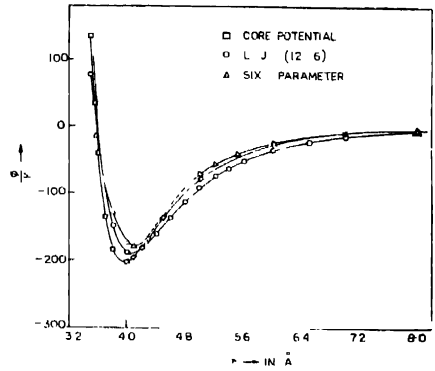

Fig. 1. Potential energy curves for krypton on different models.

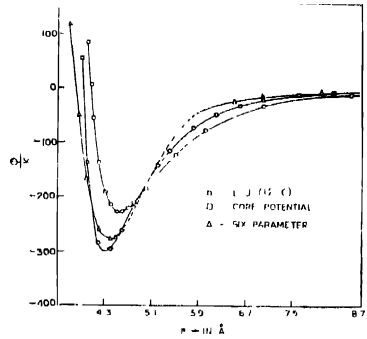

Fig. 2. Potential energy curves for xenon on different models.

From Table II it may be seen that by considering non-additive interactions it is possible to represent very satisfactorily the third virial coefficient data of krypton. The disagreement between the experimental and the calculated values of C' for xenon is quite large. One reason for this disagreement may be due to presence of krypton as an impurity in xenon. Another factor which is probably more important is that in calculating the non-additive part of C' the repulsive part of the potential has not been considered (Sherwood and Prausnitz, 1964).

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